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## Directed secondary interactions in transition metal complexes of tripodal pyrrole imine and amide ligands\*\*

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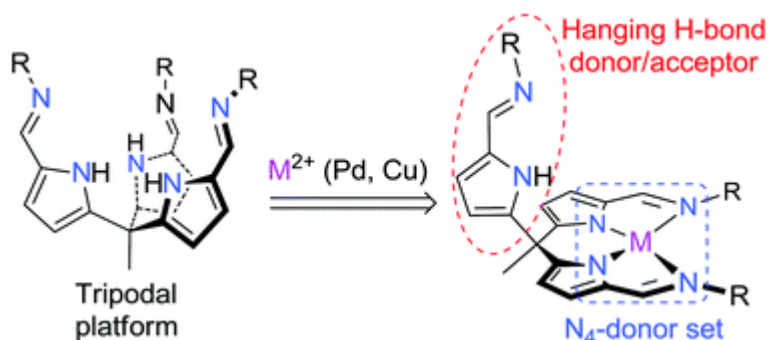
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### Supporting information:

<sup>[†]</sup>Electronic Supplementary Information (ESI) available: full experimental data and crystal data. See <http://dx.doi.org/10.1039/C2DT30539A>

### Graphical abstract:



## Abstract

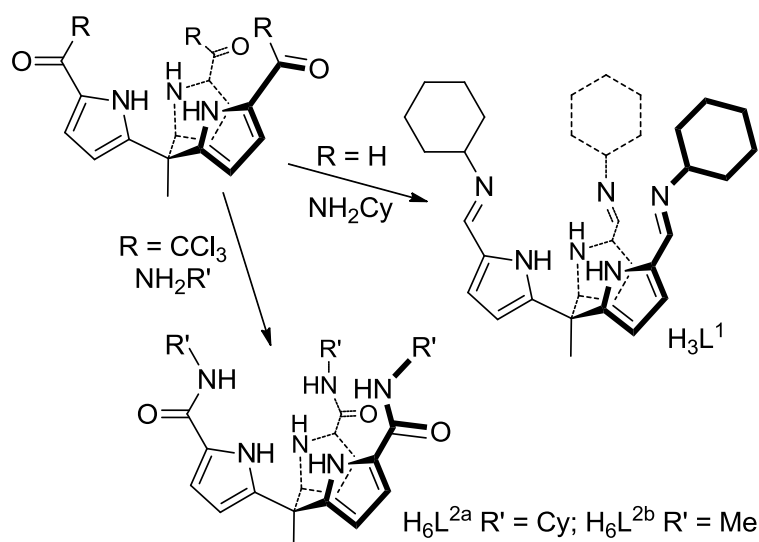
Tripodal pyrrole imine and amide ligands provide platforms for combined primary and secondary coordination sphere interactions in square planar Pd and Cu, and octahedral Ti complexes.

## Introduction

Ligand designs that can satisfy the coordinative needs of transition metals and provide peripheral functionality to stabilise and direct reactivity are becoming intrinsic to modern chemical catalysis.<sup>1</sup> This is especially apparent in the multiple proton-electron transfer reactions that are requisite for the sustainable transformations of small molecules such as O<sub>2</sub>, H<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub>.<sup>2</sup> Highly specialised ligands such as picket-fence,<sup>3</sup> crown,<sup>4</sup> Pacman,<sup>5</sup> and Hangman porphyrins,<sup>6</sup> have been developed to introduce axially positioned metal binding sites or acid-base appendages and provide correlation with the proton and electron delivery pathways found in metalloenzymes that carry out these important transformations.<sup>7</sup> Unfortunately, the multi-step synthetic routes to many of these particular ligands can be inefficient and time-consuming, so limiting their applicability. Organometallic carbene complexes which incorporate N-H donors close to the reactive metal site have also been prepared and show potential as substrate recognition motifs.<sup>8</sup>

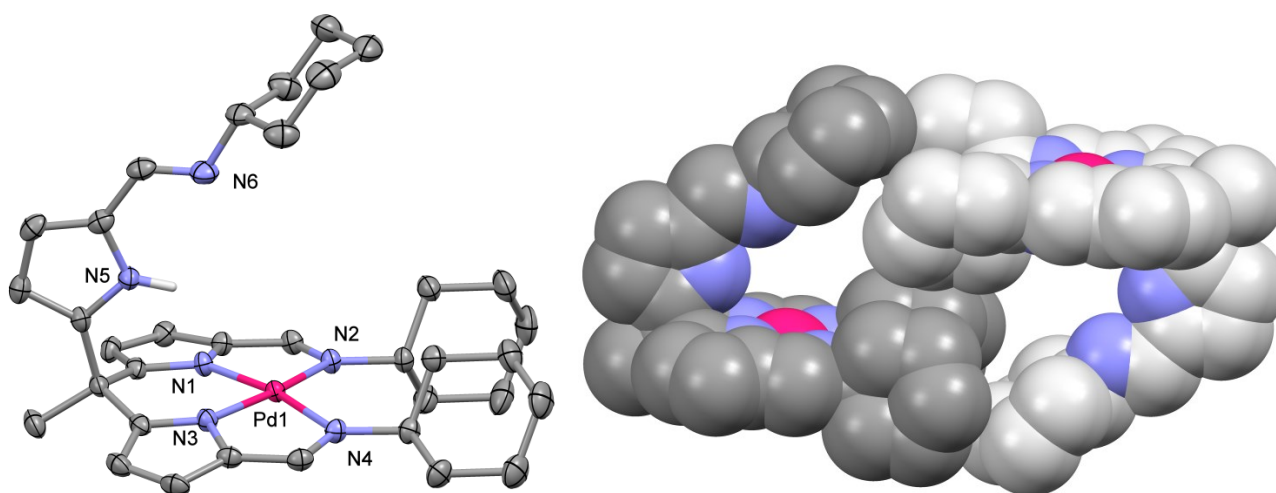
We have shown previously that Schiff-base condensation reactions favour the ready formation of flexible polypyrrolic macrocycles that form well-defined, Pacman complexes reminiscent of cofacial diporphyrins.<sup>9</sup> Monometallic uranyl complexes were prepared in which the secondary sphere can be addressed to facilitate unique reduction and functionalisation chemistry of the uranyl oxo-group.<sup>10</sup> Ditopic pyrrole-crown ether macrocycles were also prepared and form complexes in which the apical polyether acts as a hydrogen-bond acceptor and promotes supramolecular structural assembly.<sup>11</sup> Here, we report an alternative molecular design strategy in which judicious choice of the transition metal in metallation reactions of the related, and potentially tripodal pyrrole-imine ligand L<sup>1</sup>,<sup>12</sup> and its amide variant L<sup>2</sup>, results in the formation of well-defined metal complexes of porphyrin-like N<sub>4</sub>-donors in which one arm of the tripodal ligand remains available for, and involved in, secondary-sphere interactions.

The pyrrole-imine pro-ligand H<sub>3</sub>L<sup>1</sup> was synthesised according to the literature from the straightforwardly made, triply formylated tripyrrole (Scheme 1).<sup>12, 13</sup> The amide variant H<sub>6</sub>L<sup>2</sup> was prepared in two high-yielding steps from the tripyrrole that involved the formation of the 2-trichloroacetyl derivative and its subsequent nucleophilic substitution reactions with either cyclohexylamine or methylamine.<sup>14</sup> The <sup>1</sup>H NMR spectrum of H<sub>6</sub>L<sup>2a</sup> (R' = Cy) in CDCl<sub>3</sub> has characteristic pyrrole and amide N-H resonances at 10.9 and 7.78 ppm, respectively, the latter a doublet due to coupling to the methine hydrogen of the cyclohexyl substituent.



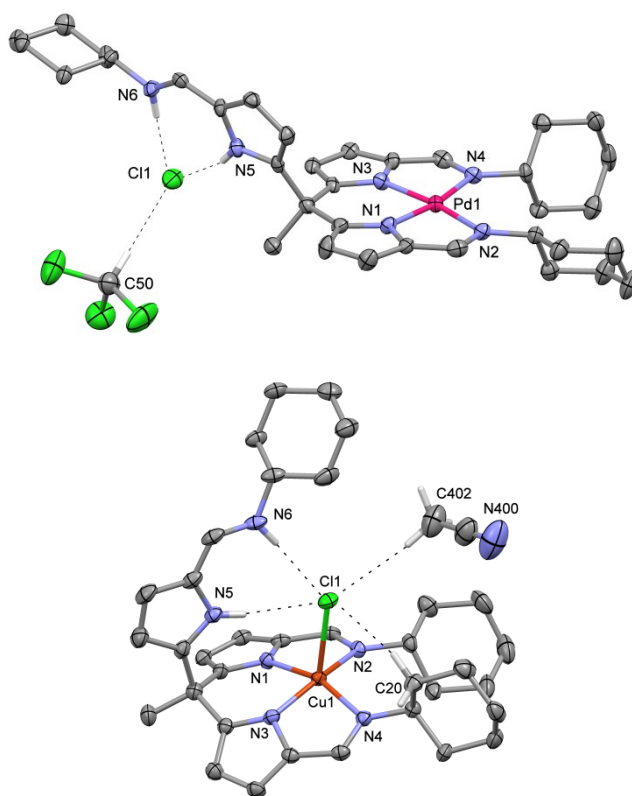
**Scheme 1.** Synthetic approaches to imine and amide donor-extended tripodal pyrroles

The reaction between pyrrole-imine  $H_3L^1$  and  $M(OAc)_2$  ( $M = Pd, Cu$ ) in MeCN led to the formation of the complexes  $[M(HL^1)]$  in good yields. In the  $^1H$  NMR spectrum of  $[Pd(HL^1)]$  in  $CDCl_3$ , it is clear that two different pyrrole-imine environments are present in a 2:1 ratio, and are consistent with two arms of the tripodal ligand coordinated to Pd while the other remains pendant. This assignment of the solution structure is supported by the solid state structure determined by X-ray crystallography (Fig. 1),<sup>‡</sup> which shows that Pd1 is bound by  $L^1$  in a square planar geometry by two of the pyrrole-imine arms of the tripodal ligand, while the third is pendant and positioned above the axial coordination site. This ligand is therefore adopting a hypodentate coordination mode similar to that seen for complexes of, for example, polydentate N-donor and scorpionate ligands in which the metal ion binds using less than the maximum number of donor atoms.<sup>15</sup> Unlike in  $[Co(H_3L^1)_2]$  and  $[Zn_2(H_2L^1)_2]$ , which adopt structures in which pyrrole-imine tautomerisation occurs to form the azafulvene-amine isomer,<sup>12</sup> the geometrical data of the pendant arm confirms that the pyrrole-imine tautomer is preferred in this case. The orientation of the arms of the tripodal ligand in  $[Pd(HL^1)]$  impacts on the extended structure in which two molecules are organised such that the hydrophobic and bulky cyclohexyl substituents interdigitate to form a dimeric motif (Fig. 1, bottom) with shortest C-C contacts of 3.74 Å. Furthermore, C-H bonds of the cyclohexyl group of the pendant arm interact with the vacant Pd axial site of an adjacent complex, with close C-C, C-N, and C-Pd contacts ranging from 3.69-3.72 Å, and which results in an infinite dimeric chain assembly in the solid state with Pd...Pd separations of 8.38 and 10.9 Å. While no crystals of the Cu analogue were grown, the ESI spectrum displayed a molecular ion at  $m/z$  650 and the solution magnetic moment of 2.23 BM supports the presence of the  $d^9$  metal centre.



**Figure 1.** Solid-state structure of  $[\text{Pd}(\text{HL}^1)]$  (left) and its space-filled representation (right). For clarity, all hydrogen atoms, except those involved in hydrogen-bonding interactions, are omitted (where shown, displacement ellipsoids are drawn at 50% probability). Selected bond lengths (Å) and angles (°): Pd1-N1 1.944(2); Pd1-N2 2.084(2); Pd1-N3 1.946(2); Pd1-N4 2.092(2);  $\sum \angle \text{Pd1} = 359.76$ .

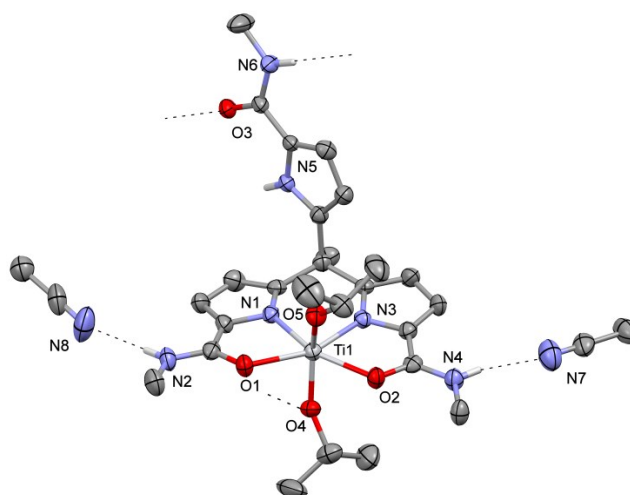
Similar reactions between the metal halide salts  $\text{MCl}_2$  ( $\text{M} = \text{Pd}, \text{Cu}$ ) and  $\text{H}_3\text{L}^1$  resulted in the ready formation of the monomeric complexes  $[\text{MCl}(\text{H}_2\text{L}^1)]$  in which the pendant arm of the tripodal ligand is protonated. Unlike the metal acetate reactions above, the addition of  $\text{NEt}_3$  did not neutralise the complex to form  $[\text{M}(\text{HL}^1)]$  complexes, which suggests that the  $\text{pK}_a$  of the imine is  $>10.8$ . The  $^1\text{H}$  NMR spectrum of  $[\text{Pd}(\text{ClH}_2\text{L}^1)]$  in  $\text{CDCl}_3$  supports Pd coordination, with two pyrrole-imine environments in a 2:1 ratio.<sup>‡</sup> In this case, both pyrrole (13.3 ppm) and imine (12.9 ppm) nitrogens are protonated, the latter resonance a multiplet due to coupling to cyclohexyl and imine CH protons. Crystals of both complexes were analysed by X-ray crystallography and the solid state structures display similar gross geometries in which the Pd or Cu metal centre is bound by two of the three pyrrole-imine arms while the third is pendant and interacts with the chloride (Fig. 2).<sup>‡</sup> In  $[\text{Pd}(\text{ClH}_2\text{L}^1)]$ , the chloride Cl1 is hydrogen-bonded to both imine and pyrrole hydrogens and a molecule of  $\text{CHCl}_3$  solvent of crystallisation and does not interact with the metal centre. In contrast, in the Cu analogue  $[\text{CuCl}(\text{H}_2\text{L}^1)]$ , Cu1 adopts a square-pyramidal geometry in which the chloride Cl1 is coordinated to Cu1 in the Jahn-Teller distorted axial position and located in an assembled hydrogen-bonding pocket comprising N-H and C-H donors from the pendant pyrrole-imine arm, a cyclohexyl group, and MeCN solvent of crystallisation. It is therefore evident that for metals that favour square planar geometries,  $\text{L}^1$  can be used to straightforwardly construct complexes which address both the primary and secondary coordination spheres, and act as platforms for combined cation and anion binding.<sup>16</sup>



**Figure 2.** Solid-state structures of  $[\text{Pd}(\text{ClH}_2\text{L}^1)](\text{CHCl}_3)$  (top) and  $[\text{CuCl}(\text{H}_2\text{L}^1)]$  (bottom). For clarity, all hydrogen atoms, except those involved in hydrogen-bonding interactions, and some solvent of crystallisation are omitted (displacement ellipsoids are drawn at 50% probability). Selected bond lengths (Å) and angles (°): (i) Pd1-N1 1.952(4); Pd1-N2 2.108(4); Pd1-N3 1.955(4); Pd1-N4 2.116(4); N5 $\cdots$ Cl1 3.175(4); N6 $\cdots$ Cl1 3.138(5); C50 $\cdots$ Cl1 3.425(6);  $\sum \angle \text{Pd1} = 359.9$ ; (ii) Cu1-Cl1 2.583(1); Cu1-N1 1.948(3); Cu1-N2 2.085(3); Cu1-N3 1.947(3); Cu1-N4 2.064(3); Cl1 $\cdots$ N5 3.270(3); Cl1 $\cdots$ N6 3.099(3); Cl1 $\cdots$ C20 3.711(5); Cl1 $\cdots$ C402 3.81(1); N1-Cu1-Cl1 99.90(8); N2-Cu1-Cl1 89.85(8).

While pyrrole-amide compounds have been keenly evaluated as receptors for anions,<sup>17</sup> they have been little used as ligands in transition metal chemistry even though the presence of the amide group would be expected to alter the structural and electronic characteristics of the complex.<sup>18</sup> As such, we carried out the protonolysis reaction between the tripodal pyrrole-amides  $\text{H}_6\text{L}^{2\text{a/b}}$  and  $\text{Ti}(\text{O}^i\text{Pr})_4$  in THF, which resulted in the clean elimination of two equivalents of  $\text{HO}^i\text{Pr}$  and the formation of  $[\text{Ti}(\text{O}^i\text{Pr})_2(\text{H}_4\text{L}^{2\text{a/b}})]$  in good yields; no further  $\text{HO}^i\text{Pr}$  elimination was observed, even at elevated temperatures.‡ In a similar manner to the imine complexes  $[\text{Pd}(\text{HL}^1)]$  and  $[\text{Pd}(\text{ClH}_2\text{L}^1)]$ , the  $^1\text{H}$  NMR spectra of both  $[\text{Ti}(\text{O}^i\text{Pr})_2(\text{H}_4\text{L}^{2\text{a/b}})]$  display two sets of resonances in a 2:1 ratio that support the coordination of two arms of the tripodal ligand to the metal, with one arm remaining pendant. This geometry is supported by the X-ray crystal structure of  $[\text{Ti}(\text{O}^i\text{Pr})_2(\text{H}_4\text{L}^{2\text{b}})]$  (Fig. 3) in which the Ti centre adopts a distorted octahedral geometry comprising a  $\text{N}_2\text{O}_2$  equatorial donor set arising from the tripodal ligand and axial  $\text{O}^i\text{Pr}$  groups.‡ The two

O<sup>i</sup>Pr groups are canted away from the pyrrolides subtending a non-linear O4-Ti1-O5 angle, presumably as a result of steric pressure from the pendant pyrrole-amide arm and the presence of MeCN hydrogen-bonded to O4 (not shown). The presence of the electropositive, oxophilic Ti metal centre results in preferential coordination of the amide group through its O-donor, and allows the amide N-H to hydrogen bond to MeCN solvent of crystallisation. In contrast to [CuCl(H<sub>2</sub>L<sup>1</sup>)], the pendant pyrrole-amide arm in [Ti(O<sup>i</sup>Pr)<sub>2</sub>(H<sub>4</sub>L<sup>2b</sup>)] does not interact with the axial O-ligands but instead forms N-H···O hydrogen-bonds to a neighbour which results in an infinite linear zig-zag motif in the the solid state.



**Figure 3.** Solid-state structure of [Ti(O<sup>i</sup>Pr)<sub>2</sub>(H<sub>4</sub>L<sup>2b</sup>)](MeCN)<sub>2</sub> (R' = Me). For clarity, all hydrogen atoms, except those involved in hydrogen-bonding interactions, are omitted (displacement ellipsoids are drawn at 50% probability). Selected bond lengths (Å) and angles (°): Ti1-O1 2.104(4); Ti1-O2 2.104(4); Ti1-N1 2.060(4); Ti1-N3 2.065(4); Ti1-O4 1.806(3); Ti1-O5 1.794(3); N2···N8 2.934(7); N4···N7 3.040(7); O3···N6' 2.793(7); O1-Ti1-O2 128.1(1); O4-Ti1-O5 150.3(2); O1-Ti1-N1 76.1(1); O2-Ti1-N3 76.5(2); N1-Ti1-N3 79.3(1).

We have shown that the primary and secondary spheres in complexes of the pyrrole-imine ligand L<sup>1</sup> and the pyrrole-amide ligand L<sup>2</sup> can be managed through judicious choice of metal. For L<sup>1</sup>, square planar Cu<sup>II</sup> and Pd<sup>II</sup> cations favour a porphyrin-like N<sub>4</sub>-donor set made up of two of the three arms of the potentially tripodal ligand, thus leaving one arm pendant and able to define the acid-base characteristics of the secondary sphere environment. A similar structural motif is favoured in a Ti alkoxide complex of L<sup>2</sup>, and suggests that the formation of truly tripodal complexes of these ligands is generally inhibited, with the N<sub>4</sub>- or N<sub>2</sub>O<sub>2</sub> square-planar donor environments dominant. We are currently evaluating the impact of the pendant pyrrole imine and amide functionalities on the secondary sphere chemistry of these complexes, and are investigating routes to the cyclisation of the square-planar donor set to facilitate complexation of a range of metals.

## Notes and references

‡Representative synthetic and crystal data:

[Pd(HL<sup>1</sup>)] yellow solid in 62 % yield (0.39 g). Analysis. Found: C, 63.81; H, 6.93; N, 12.67 % C<sub>35</sub>H<sub>46</sub>N<sub>6</sub>Pd requires C, 63.96, H, 7.05, N, 12.79 %. Single crystals were grown by cooling a saturated MeCN solution: C<sub>35</sub>H<sub>46</sub>N<sub>6</sub>Pd, *M* 657.18, triclinic *P*−1, *a* = 11.6995(6), *b* = 13.0619(7), *c* = 13.1928(7) Å,  $\alpha$  = 115.965(5),  $\beta$  = 113.289(5),  $\gamma$  = 94.036(4)°, *V* 1590.89(15) Å<sup>3</sup>, 150(2) K, *Z* = 2, 7757 independent reflections, *R*(int) 0.047, *R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] 0.032, CCDC 866705.

[Pd(ClH<sub>2</sub>L<sup>1</sup>)] yellow solid in 60 % yield (0.075 g). Analysis. Found: C, 60.47; H, 6.68; N, 11.92 % C<sub>35</sub>H<sub>47</sub>ClN<sub>6</sub>Pd requires C, 60.60, H, 6.83, N, 12.12 %. Single crystals were grown by slow diffusion of hexane into a saturated CH<sub>2</sub>Cl<sub>2</sub> solution: C<sub>36</sub>H<sub>48</sub>Cl<sub>4</sub>N<sub>6</sub>Pd, *M* 813.00, monoclinic *P*2<sub>1</sub>/*c*, *a* = 17.130(2), *b* = 11.0690(14), *c* = 20.818(3) Å,  $\alpha$  =  $\gamma$  = 90,  $\beta$  = 108.888(14)°, *V* 3734.7(8) Å<sup>3</sup>, 150(2) K, *Z* = 4, 4544 independent reflections, *R*(int) 0.057, *R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] 0.042, CCDC 866706.

[CuCl(H<sub>2</sub>L<sup>1</sup>)] Green solid in 65 % yield (0.37 g). Analysis. Found: C, 64.64; H, 7.32; N, 12.84 % C<sub>35</sub>H<sub>47</sub>CuClN<sub>6</sub> requires C, 64.59, H, 7.28, N, 12.91 %. Single crystals were grown by slow diffusion of Et<sub>2</sub>O into a saturated MeCN solution: C<sub>75.25</sub>H<sub>105.75</sub>Cl<sub>2</sub>Cu<sub>2</sub>N<sub>12.5</sub>O, *M* 1399.45, orthorhombic *Pna*21, *a* = 16.9395(3), *b* = 16.1910(3), *c* = 26.7675(5) Å,  $\alpha$  =  $\beta$  =  $\gamma$  = 90°, *V* 7341.5(2) Å<sup>3</sup>, 150(2) K, *Z* = 4, 14997 independent reflections, *R*(int) 0.041, *R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] 0.046, CCDC 866707.

[Ti(O<sup>*i*</sup>Pr)<sub>2</sub>(H<sub>4</sub>L<sup>2b</sup>)] colourless solid in 66 % yield (0.13 g). Analysis. Found: C, 56.01; H, 6.37; N, 15.18 % C<sub>26</sub>H<sub>35</sub>N<sub>6</sub>O<sub>5</sub>Ti requires C, 55.72, H, 6.47, N, 14.99 %. Single crystals were grown by slowly cooling a saturated MeCN solution: C<sub>32</sub>H<sub>45</sub>N<sub>9</sub>O<sub>5</sub>Ti, *M* 683.67, monoclinic *P*2<sub>1</sub>/*c*, *a* = 11.704(10), *b* = 35.30(3), *c* = 9.483(12) Å,  $\alpha$  =  $\gamma$  = 90,  $\beta$  = 112.407(12)°, *V* 3622(7) Å<sup>3</sup>, 160(2) K, *Z* = 4, 6022 independent reflections, *R*(int) 0.124, *R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] 0.087, CCDC 866708.

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